Polarography of Aromatic Diazonium Salts

## BY JAY K. KOCHI

Several aromatic diazonium salts have been studied polarographically. An attempt has been made to correlate half-wave potentials with substituent effects.

Aromatic diazonium salts represent a class of compounds which is potentially amenable to the study of substituent effects in reductions at the dropping mercury electrode. The study is facilitated by the solubility of these compounds in water and the relatively low potentials at which they are reducible.[1,2] The polarograms of these compounds show two well-defined waves at approximately -0.2 and -1.0 volts vs. S.C.E. It has been shown for some compounds that the lower wave is pH independent while the second wave is pH dependent. There appears to be some disagreement[2,3] as to the number of electrons involved in each step. We have re-examined these reductions and have found by coulometric analyses that, in fact as Atkinson, et al., found for benzenediazonium ion, the first wave corresponds to a one-electron reduction and the second wave to a two-electron reduction. The first wave is pH independent and the i_d/C ratio remains virtually constant through the pH ranges studied. The second wave, however, as found earlier,[1-3] is pH dependent. The variation in the half-wave potential is linear with the pH of the medium and corresponds to roughly 0.05 volt per pH unit. In view of the apparent complexity of this wave we have restricted ourselves to the first wave.

From the available data it appears that the most reasonable processes for the first wave correspond to

$$ArN_2^+ + e^- \longrightarrow ArN_2\cdot \qquad \text{(a)}$$
$$ArN_2^+ + e^- \longrightarrow Ar\cdot + N_2 \qquad \text{(b)}$$
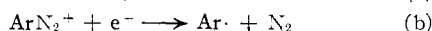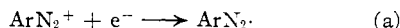
Process (b) appears unlikely in view of the composition of the material gathered at the cathode during controlled potential reductions. We have been unable to detect the presence of any diaryl or aromatic hydrocarbons in addition to diaryl mercury compounds and aryl mercuric chlorides previously reported.[1] The large amount of tarry material from which these compounds are separated contains a fair amount of nitrogen. For example, the decomposition of benzenediazonium chloride leads to non-homogeneous tars which, after extraction of the mercury compounds, gives an approximate analysis for $C_6H_5N_2$. The mercuric compounds may very well arise from a secondary reaction between ArN_2 radical and the mercury cathode. In view of these observations the reaction potentials of the first wave will be interpreted in this paper on the assumption that the primary electrode process is given by mechanism (a).

The information regarding the change in half-

wave potentials of the first wave as a function of the substituent groups appeared to be of interest In particular, if the process is formulated as
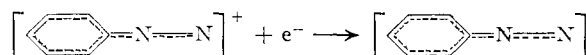
then it would seem that there may be an interesting variation in the electronic properties of the diazo cation and diazo radical.

Experimental

Apparatus.—A Sargent–Heyrovsky Model XI polarograph was used in all the determinations. The temperature was maintained at $0.2 \pm 0.1°$ by means of a crushed ice–water slurry which was constantly stirred except during the measurements. A single capillary with $t = 3.5$ sec. and a capillary constant, $m^{2/3}t^{1/6}$, equal to 2.32 mg.$^{2/3}$ sec.$^{-1/2}$ was used in all the runs. The Lingane–Laitinen H-cell[4] was modified slightly to accommodate an external saturated calomel anode which was maintained at room temperature. It was connected to the H-cell by means of a short 15 mm. diameter saturated potassium chloride agar bridge.

Controlled potential reductions were done with the apparatus described by Lingane and Jones[5] at -0.3 volt vs. S.C.E. with p-chlorobenzenediazonium, p-methoxybenzenediazonium and benzenediazonium chlorides using an hydrogen–oxygen coulometer. In an average of five determinations each, the electron consumption varied from 0.90 to 1.10 electrons per diazonium ion. The second wave was investigated with p-chlorobenzenediazonium chloride only. Our results corroborrated those by Atkinson, et al.[1,3] The tarry material which collected at the cathode was extracted with petroleum ether (b.p. 30–60°) in which chlorobenzene, anisole and benzene and the diaryls are soluble. Careful distillation of the solvent followed by nitration of the residue gave no identifiable products[6] aside from small amounts of the previously mentioned mercury compounds which are partially soluble in this solvent. The mercury compounds were isolated from the tar by the method described by Atkinson.[1]

Preparation of Diazonium Salts.—Benzenediazonium and m-bromobenzenediazonium chlorides were prepared by the method of Crossley, Kienle and Benbrook.[7] The material was recrystallized twice from absolute ethanol-ether mixtures and yielded colorless platelets.

Anal. Calcd. for $C_6H_5N_2Cl$: Cl, 25.2. Found[8]: Cl, 25.0. $C_6H_4N_2BrCl$: Cl, 16.1. Found: Cl, 16.1.

The bisulfates of p-nitrobenzenediazonium, p-methoxybenzenediazonium, p-methylbenzenediazonium and benzenediazonium ions were made in ethanol–sulfuric acid solutions with amyl nitrite.[9] They crystallized as colorless platelets from either absolute methanol or mixtures of methanol and ethanol.

(1) E. R. Atkinson, H. Warren, P. Abell and R. Wing, THIS JOURNAL, **72**, 915 (1950).

(2) R. Elofson, R. Edsberg and P. Mecherly, J. Electrochem. Soc., **97**, 166 (1950).

(3) E. R. Atkinson, C. Garland and R. Butler, THIS JOURNAL, **75**, 983 (1953).

(4) J. J. Lingane and H. A. Laitinen, Anal. Chem., **11**, 504 (1939).

(5) J. J. Lingane and S. L. Jones, ibid., **22**, 1169 (1950); J. J. Lingane, 'Electroanalytical Chemistry,'' Interscience Publishers, New York, N. Y., 1953, p. 349.

(6) R. L. Shriner and R. C. Fuson, "Identification of Organic Compounds," 3rd Ed., John Wiley and Sons, Inc., New York, N. Y., 1945, p. 197.

(7) M. L. Crossley, R. H. Kienle and C. H. Benbrook, THIS JOURNAL, **62**, 1400 (1940).

(8) Chloride titrations were done potentiometrically with standard silver nitrate solutions using a silver–silver chloride electrode and a Beckman Model G pH meter.

(9) E. Knoevenagel, Ber., **28**, 2048 (1895).

Anal. Calcd. for $C_6H_5N_3O_6S$: S, 13.0. Found[10]: S, 12.8. $C_7H_8N_2O_5S$: S, 13.8. Found: S, 13.5. $C_7H_8N_2O_4S$: S, 14.8. Found: S, 14.7. $C_6H_6N_2O_4S$: S, 15.8. Found: S, 15.5.

m-Nitrobenzenediazonium bisulfate could not be crystallized by the Knoevenagel procedure. It was prepared in acetic–sulfuric acid mixtures using a variation of the Hodgson and Mahadevan method[11] with butyl nitrite. Recrystallization from methanol–ethanol mixtures yielded colorless crystalline material.

Anal. Calcd. for $C_6H_5N_3O_6S$: S, 13.0. Found: S, 12.9.

Sulfanilic acid was diazotized by the usual procedure with sodium nitrite and dilute sulfuric acid. It was washed repeatedly with water until colorless and used as such.

p-Aminobenzoic acid in sulfuric acid was diazotized with butyl nitrite in glacial acetic acid. It was precipitated with acetone and recrystallized twice as the bisulfate from methanol.

Anal. Calcd. for $C_7H_6N_2O_6S$: S, 13.0. Found: S, 12.7.

Buffer Solutions.—Buffer solutions[12] were made up at *p*Hs of approximately 1, 2, 4, 6 and 8. In order to test the independence of polarograms on buffers, two buffers of different composition were prepared at each *p*H. Listed below are the buffers used and their *p*H values (determined directly with a Beckman Model G *p*H meter). Potassium chloride was added to each buffer to bring the ionic strength up to 0.5.

Walpole-acetate, 1.36; Walpole-acetate, 2.13, Clark and Lubs-phthalate, 2.20; Walpole-acetate, 4.12, Clark and Lubs-phthalate, 3.82; Clark and Lubs-phthalate, 5.83; Clark and Lubs-phosphate, 5.81; Clark and Lubs-borate, 7.94; Clark and Lubs-phosphate, 7.94.

No difference in the polarographic behavior could be detected for any pair of buffers at a given *p*H for the whole series of compounds tested.[13]

Polarography.—Polarograms were taken on solutions which had been deaerated at 0.2° for at least ten minutes. From knowledge of polarograms taken at various lengths of time it appears that all the diazonium solutions are stable at this temperature for periods of least one hour. In solutions of higher *p*Hs the solutions turn yellow to orange and except for a few cases determinations were not made at *p*Hs greater than 8. At *p*Hs of 9 or greater all the diazonium solutions showed abnormal behavior. The solutions were made by adding 20 ml. of buffer solution and 1 ml. of a 0.1% gelatin solution to the H-cell. After temperature equilibration and deaeration for ten minutes, standard deaerated diazonium stock solution was pipetted in; the solution was made up to 25 ml. by the addition of water. The length of further deaeration depended on the *p*H of the buffer. It was found that the maximum suppressor was ineffective in optimal concentrations when the diazonium solution exceeded 2 millimolar as reported by Atkinson, *et al.*[1]

Results

In all cases studied with the exception of *p*-carboxybenzenediazonium, *m*-nitrobenzenediazonium and *p*-nitrobenzenediazonium bisulfate two distinct waves were obtained. The values of the half-wave potentials of the first wave together with the diffusion currents per unit concentration are listed in Table I. As stated previously the second wave appeared to be too complex to study with any consistency. Two features, however, stand out. First, the variations in the half wave value with *p*H of the solution is distinctly linear. The slope of the line in

(10) Sulfur was determined as barium sulfate utilizing the procedure, found in I. M. Kolthoff and E. B. Sandell, "Textbook of Quantitative Inorganic Analysis," Third Ed., The Macmillan Co., New York, N. Y., 1953.

(11) H. H. Hodgson and A. P. Mahadevan, *J. Chem. Soc.*, 325 (1947).

(12) H. T. Britton, "Hydrogen-Ions," Vol. I, Chapman and Hall, Ltd., 1942, p. 300 ff.; I. M. Kolthoff, "Acid-Base Indicators," The Macmillan Co., New York, N. Y., 1937, p. 239 ff.

(13) K. G. Stone, *J. Electrochem. Soc.*, **97**, 63 (1950); J. C. Komyathy, R. E. VanAtta, C. S. Tang and I. Rosenthal, *Anal. Chem.*, **23**, 1218 (1951).

all cases is uniformly 0.05 volt per *p*H unit; secondly, the diffusion current for the second wave is nearly three times that of the first wave and does not, therefore, correspond to a linear variation in the number of electrons transferred in this step.[3] In none of our diazonium salts could we detect a measurable wave below 0 volt *vs.* S.C.E. With *p*-methylbenzenediazonium bisulfate and *m*-bromobenzenediazonium chloride the first wave appeared at first to be a doublet; several more recrystallizations of the diazonium salts, however, removed this anomaly.

When polarograms were obtained in acetone–water mixtures the half-wave potentials were shifted toward more negative values. For example, the half-wave potential of benzenediazonium chloride shifted from -0.188, -0.193, -0.210, to -0.220 volt *vs.* S.C.E. on changing the medium from 0, 20, 40 and 60% acetone in water. The shift was not sufficient to merit further study.[14]

In the case of *p*-carboxybenzenediazonium ion the diffusion current decreased with increasing *p*H with a concomitant increase in the second wave (also changing with *p*H). The break in the diffusion current *vs.* *p*H curve occurred at a *p*H of approximately 4–6. This value probably corresponds to the ionization constant of the *p*-carboxybenzenediazonium ion. It is interesting to note that both *m*- and *p*-nitrobenzenediazonium ions have approximately the same half-wave values at the various *p*Hs. Moreover the $E_{1/2}$s vary linearly with the *p*H of the solutions in a manner similar to the second wave of the other compounds. The unexpected behavior of this pair of compounds suggests that it is the nitro group and not the diazonium group which is undergoing reduction. The reduction of

TABLE I

HALF-WAVE POTENTIALS[a] FOR THE FIRST WAVE OF AROMATIC DIAZONIUM SALTS

Compound	Buffer solutions				
	1	2	4	6	8
p-Carboxybenzenedia-zonium bisulfate	0.155 (1.70)	....	0.152 (1.54)	0.159 (0.54)	0.160 (0.22)
Diazotized sulfanilic acid	0.273 (1.87)	....	0.270 (1.55)	0.273 (1.41)	0.275 (1.41)
p-Methylbenzenedia-zonium bisulfate	0.155 (1.81)	....	0.153 (1.76)	....	0.145 (1.72)
Benzenediazonium bisulfate	0.181 (1.45)	....	0.188 (1.48)	....	0.182 (1.41)
p-Methoxybenzene-diazonium bisulfate	0.118 (2.18)	0.105 (2.11)	0.116 (2.14)	0.117 (2.17)	0.110 (2.13)
m-Nitrobenzene-diazonium bisulfate	0.182 (3.1)	....	0.366 (8.5)	0.436 (8.0)	0.546 (7.8)
p-Nitrobenzene-diazonium bisulfate	0.163 (3.6)	0.236 (10.5)	0.300 (9.2)	0.400 (8.5)	0.500 (8.3)
m-Bromobenzene-diazonium chloride	0.168 (1.34)	....	0.162 (1.32)	0.160 (1.31)	0.165 (1.34)
p-Chlorobenzene-diazonium bisulfate	....	....	0.179 (1.24)	0.175 (1.28)	0.166 (1.23)
Benzenediazonium chloride	0.188 (1.48)	0.185 (1.48)	0.190 (1.50)	0.194 (1.50)	0.185 (1.45)

[a] Values are given in negative volts *vs.* S.C.E. and are significant to two figures. Values in parentheses represent the diffusion current per unit of concentration, i_d/C, expressed as microamperes in millimolar solutions of diazonium salts.
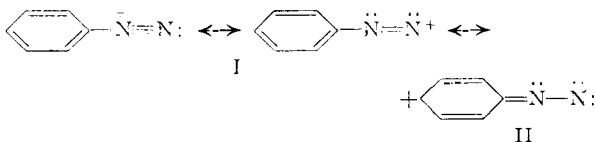
(14) (a) O. D. Shreve and E. C. Markham, THIS JOURNAL, **71**, 2993 (1949); (b) J. E. Page, J. W. Smith and J. G. Waller, *J. Phys. Colloid Chem.*, **53**, 545 (1949).

the nitro group is pH dependent and usually undergoes reduction at higher potentials.[15,14b]

Discussion

Some attempts have been made in the past to relate polarographic half-wave values with some function of the substituent group.[16] The majority of the cases employed for this type of study suffer from the disadvantage of (a) dependence on hydrogen ion concentration and (b) involving more than one electron. The first halves of the polarographic reduction of diazonium ions are singularly free of these complications, the wave being (a) pH independent, (b) i_d/C constant and (c) composed of a one-electron transfer. To the contrary notwithstanding, in the absence of more exact knowledge of the mechanism of the electrode process, the half-wave values will be analyzed as though they were reversible waves, and subsequent reactions did not affect them.[17]
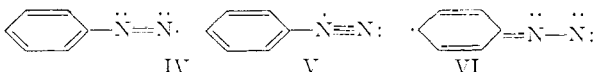
If we consider the diazonium ion a resonance hybrid of the electron configurations I and II
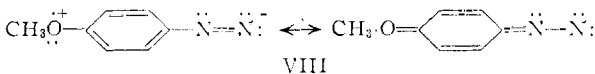
$$\langle\hspace{-0.3em}\bigcirc\hspace{-0.3em}\rangle-\ddot{N}\!\!=\!\!N: \longleftrightarrow \langle\hspace{-0.3em}\bigcirc\hspace{-0.3em}\rangle-\ddot{N}\!\!=\!\!\ddot{N}^+ \longleftrightarrow$$

I

$$+\langle\hspace{-0.3em}\bigcirc\hspace{-0.3em}\rangle\!\!=\!\!\ddot{N}\!\!-\!\!\ddot{N}:$$

II

then it may be expected that such substituents as p-methoxy or p-dimethylamino and to a lesser extent, p-methyl, would stabilize the ion by virtue of increasing the contribution from form II as in III[18]

$$CH_3\overset{+}{O}\!\!=\!\!\langle\hspace{-0.3em}\bigcirc\hspace{-0.3em}\rangle\!\!=\!\!\ddot{N}\!\!-\!\!\ddot{N}: \quad III$$
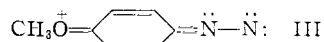
The electronic requirements of the diazo radical on the other hand, may be different

$$\langle\hspace{-0.3em}\bigcirc\hspace{-0.3em}\rangle-\ddot{N}\!\!=\!\!\ddot{N}\cdot \quad \langle\hspace{-0.3em}\bigcirc\hspace{-0.3em}\rangle-\ddot{N}\!\!=\!\!N: \quad \cdot\langle\hspace{-0.3em}\bigcirc\hspace{-0.3em}\rangle\!\!=\!\!\ddot{N}\!\!-\!\!\ddot{N}:$$

IV   V   VI

In order to get aid from substituents like alkyl, hyperconjugated structures like VII, and for methoxyl, structures like VIII must be postulated[19]

$$\cdot H\ CH_2\!\!=\!\!\langle\hspace{-0.3em}\bigcirc\hspace{-0.3em}\rangle\!\!=\!\!\ddot{N}\!\!-\!\!\ddot{N}:$$

VII

$$CH_3\overset{\cdot+}{O}\!\!-\!\!\langle\hspace{-0.3em}\bigcirc\hspace{-0.3em}\rangle\!\!-\!\!\ddot{N}\!\!=\!\!\ddot{N}: \longleftrightarrow CH_3\!\cdot\!O\!\!=\!\!\langle\hspace{-0.3em}\bigcirc\hspace{-0.3em}\rangle\!\!=\!\!\ddot{N}\!\!-\!\!\ddot{N}:$$

VIII

With halogen substituents it is unlikely that structures analogous to VII and VIII contribute significantly to the diazo hybrid radical.

Our experiments indicate that resonance forms like VI contribute significantly to the hybrid diazo radical. The experiments point out, further, that considerations like the determination of relative electron densities[16b] in the diazo group are not fruitful in a simple one-electron reduction. The particularly low values for the reduction potentials of p-carboxybenzenediazonium, p-methylbenzenediazonium and p-methoxybenzenediazonium ions seem to indicate that contributions from structures like VI, VII, VIII and IX play significant roles in the

$$\begin{matrix}\cdot O \\ \diagup \\ HO\end{matrix}\!\!C\!\!=\!\!\langle\hspace{-0.3em}\bigcirc\hspace{-0.3em}\rangle\!\!=\!\!N\!\!-\!\!\ddot{N}: \quad IX$$

diazo radicals. It is difficult to assess unequivocally the relative contributions from these structures especially in view of the large contribution one may get from forms like III[20,21] to the hybrid cation. If this is so, we can account for our low value of $E_{1/2}$ for the p-methoxy group by ascribing an electron configuration such as VIII an important role[22] in the hybrid diazo radical.[23] This postulate is further strengthened by the effect of the p-carboxyl group which should show lower $E_{1/2}$ values on the basis of a sole consideration of the dispersal of the electron in the diazo radical. It is unfortunate that values for the p-nitro group cannot be determined. As expected the ionized p-sulfo group (in diazotized sulfanilic acid) shows an extremely large negative reduction potential due to the presence of a negative pole. These arguments would be strengthened by a consideration of the meta isomers.[24]

It is interesting to note that the order of half-wave potentials in the one-electron reduction of diazonium ions roughly parallels the calculated order of reactivity of substituted benzene derivatives to homolytic substitutions.[25-27] The calculations were essentially based on a consideration of the stability of an intermediate like X and predicted that all substituents, R, would decrease the energy of this intermediate with respect to the unsubstituted case.

$$R\!\!-\!\!\langle\hspace{-0.3em}\bigcirc\hspace{-0.3em}\rangle\!\!\overset{\diagup H}{\underset{\diagdown X}{\cdot}} \quad X$$

(15) I. Bergman and J. C. James, Trans. Faraday Soc., 48, 956 (1952); S. F. Dennis, A. S. Powell and M. J. Astle, THIS JOURNAL, 71, 1184 (1949).
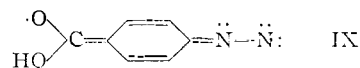
(16) (a) P. Zuman, Collection Czechoslav. Chem. Communs., 19, 599 (1954); (b) E. Gergely and T. Iredale, J. Chem. Soc., 3226 (1953); (c) S. Koide and R. Motoyama, J. Electrochem. Soc., Japan, 20, 314 (1952); (d) J. E. Page, Quart. Revs., 6, 262 (1952); (e) S. Wawzonek in I. M. Kolthoff and J. J. Lingane, "Polarography," Vol. II, Interscience Publishers, New York, N. Y., 1952; (f) E. L. Colichman and S. K. Liu, THIS JOURNAL, 76, 913 (1954).

(17) Dr. D. M. H. Kern has kindly pointed out that even if process (a) were reversible the subsequent irreversible loss of nitrogen would affect the half-wave potentials by affecting the concentration of the radicals (particularly if the decay of the diazo radical was rapid).

(18) E. S. Lewis and E. B. Miller, THIS JOURNAL, 75, 431 (1953).

(19) C. G. Overberger and A. Lebovitz, ibid., 76, 2723 (1954).

(20) There are good indications from the data on decompositions of diazonium salts that III may be an important contributor to the hybrid ion. See ref. 7 and private communication, E. S. Lewis, Rice Institute.

(21) L. H. Anderson and J. W. Steedley, THIS JOURNAL, 76, 5145 (1954), have assigned p-quinonoid structures to amino diazonium salts on the basis of spectroscopic comparisons.

(22) It has been reported (W. S. Johnson, J. M. Anderson and W. E. Shelberg, ibid., 66, 218 (1944)) that 6-methoxytetralin reacts with lead tetraacetate to give 62% yield of 1-acetoxy-6-methoxy-tetralin as the only product.

(23) Baughan, Evans and Polyani have indicated, however, that hyperconjugation forms of the carbonium ion are more important than in the corresponding radical. E. G. Baughan, M. G. Evans and M. Polanyi, Trans. Faraday Soc., 37, 377 (1941).

(24) Atkinson, et al.,[1] report values of -0.19, -0.08 and -0.09 volt vs. S.C.E. at pH 6.7 and -0.11, -0.09, and -0.05 at pH 3.6 for the diazonium salts of o-aminobenzoic, m-aminobenzoic and p-aminobenzoic acids, respectively.

(25) G. Wheland, THIS JOURNAL, 64, 907 (1942); C. Coulson, Research, 4, 307 (1951).

(26) R. D. Brown, Quart. Revs., 6, 63 (1952); M. J. Dewar, J. Chem. Soc., 463 (1949).

(27) There have been other cases reported in the literature in which most substituents lower the reduction potential with respect to hydrogen (see ref. 16b).

These predictions have been experimentally borne out recently by Hey and co-workers[28] and others. These workers have studied the homolytic reactivity of various benzene derivatives to attack by phenyl radicals and have found that, in fact, as predicted the reactivity postulated by Wheland and others is valid.[29] This work on the relative energies of the intermediates in homolytic aromatic substitutions is consistent with the half-wave values of the postulated intermediates, XI, obtained in the polarography of diazonium salts.

$$R\text{—}\langle\ \cdot\ \rangle\text{=}N\text{=}N \qquad XI$$
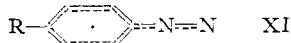
A much more complete description of the reduc-

(28) D. H. Hey and G. H. Williams, *Disc. Faraday Soc.*, **14**, 216 (1953); D. H. Hey, R. R. Augood and G. H. Williams, *J. Chem. Soc.*, 2094 (1952), 3412 (1953); R. L. Dannley and M. Sternfeld, THIS JOURNAL, **76**, 4543 (1954) and earlier papers.

(29) The relevance of these experiments may be in doubt in view of recent discoveries regarding radical complexes in solution. See C. R. Boozer and G. S. Hammond, THIS JOURNAL, **76**, 3861 (1954).

tions postulated in equation (a)[30] must await further intensive efforts to determine the reversibility or to eliminate the possibility of rate-controlled limiting currents[31] in the first polarographic waves. A study of the slope $i(i_d - i)$ is at present inconclusive.[32] Perhaps a more definitive test would be made by the method of oscillographic polarography. At this point we can only emphasize the necessarily qualitative nature of our arguments. Quantitative correlations between substituent effects and some polarographic property cannot be too enthusiastically pursued, especially in cases where the mechanism of the electrode process is not definitely known.

(30) We have not completely eliminated the possibility of equation (b) being the process for the first wave. The rationale for the stabilization of the various radicals may apply equally well to the substituted phenyl radicals. See S. G. Cohen and C. H. Wang, THIS JOURNAL, **75**, 5594 (1953).

(31) P. Delahay, *ibid.*, **73**, 4944 (1951).

(32) I. M. Kolthoff and J. J. Lingane, "Polarography," Vol. I, Interscience Publishers, New York, N. Y., 1952.

CAMBRIDGE, MASS.

NOTES

The Vapor Pressure of Polonium

BY LEROY S. BROOKS[1]

The vapor pressures of polonium between 0.3 and 90 mm. with corresponding temperatures of 438° and 745° have been measured by the method[2] employed to measure the vapor pressure of two other sixth-group elements, selenium and tellurium.

Experimental

Sample Preparation.—Polonium was vacuum-distilled seven times, reduced in a dry hydrogen atmosphere, and distilled into a quartz sample tube. The sample tube was attached to the vapor pressure apparatus which was outgassed for 48 hours at 780° while it was being evacuated to a pressure of 10^{-8} mm. The sample tube was opened to the vacuum system, the accumulated helium from the alpha decay was pumped off, and the polonium was volatilized into the sample bulb of the vapor pressure apparatus.

Pressure Measurement.—The temperature of the sickle gage was maintained at 770° during all of the measurements. During each set of measurements, the null position of the gage, which had a sensitivity of 0.03 mm. pressure per scale division deflection of the gage pointer, changed an amount equivalent to about 1 mm. The null position for each vapor pressure measurement was recorded as though the gage had drifted uniformly with time.

Temperature Measurement.—At the time of each pressure measurement, temperature measurements of the sample bulb containing the polonium and a copper block around the sample bulb revealed a temperature difference due to the energy from the decay of the polonium. This difference was about 6° at 400°, 4° at 580° and 2° at 740°. This difference decreased as the temperature increased because some of the polonium volatilized from the sample bulb to the gage.

(1) Ford Motor Company, Ford Scientific Laboratory, Dearborn, Michigan.
(2) L. S. Brooks, THIS JOURNAL, **74**, 227 (1952).

Results

The least-squares representation of nine measurements of vapor pressures between 438 and 745° is

$$\log p = \frac{-5377.8 \pm 6.7}{T} + 7.2345 \pm 0.0068$$

when p is the pressure in mm., T is the absolute temperature, and the probable errors are as stated. These measurements were taken the first two days. Due to the decay products of the polonium or an impurity, measurements on the fourth, fifth, sixth and eighth days gave a lower vapor pressure curve each day.

From the above equation, the calculated boiling point is 962.04 ± 1.93°C. and the latent heat of vaporization is 24.597 ± 0.031 kcal./mole.

MOUND LABORATORY[3]
MONSANTO CHEMICAL COMPANY
MIAMISBURG, OHIO

Iodine Solutions of Unexpected Color

BY ERVIN COLTON

It is well known that iodine in "non-active" solvents yields *violet* solutions[1] with an absorption maximum in the proximity of 520 mμ. In these solvents the iodine dissolves without reaction. Table I lists the absorption for iodine in three "non-active" solvents.

(1) J. Kleinberg and A. W. Davidson, *Chem. Revs.*, **42**, 601 (1948).